Passive sampling: effective sensing of environmental quality

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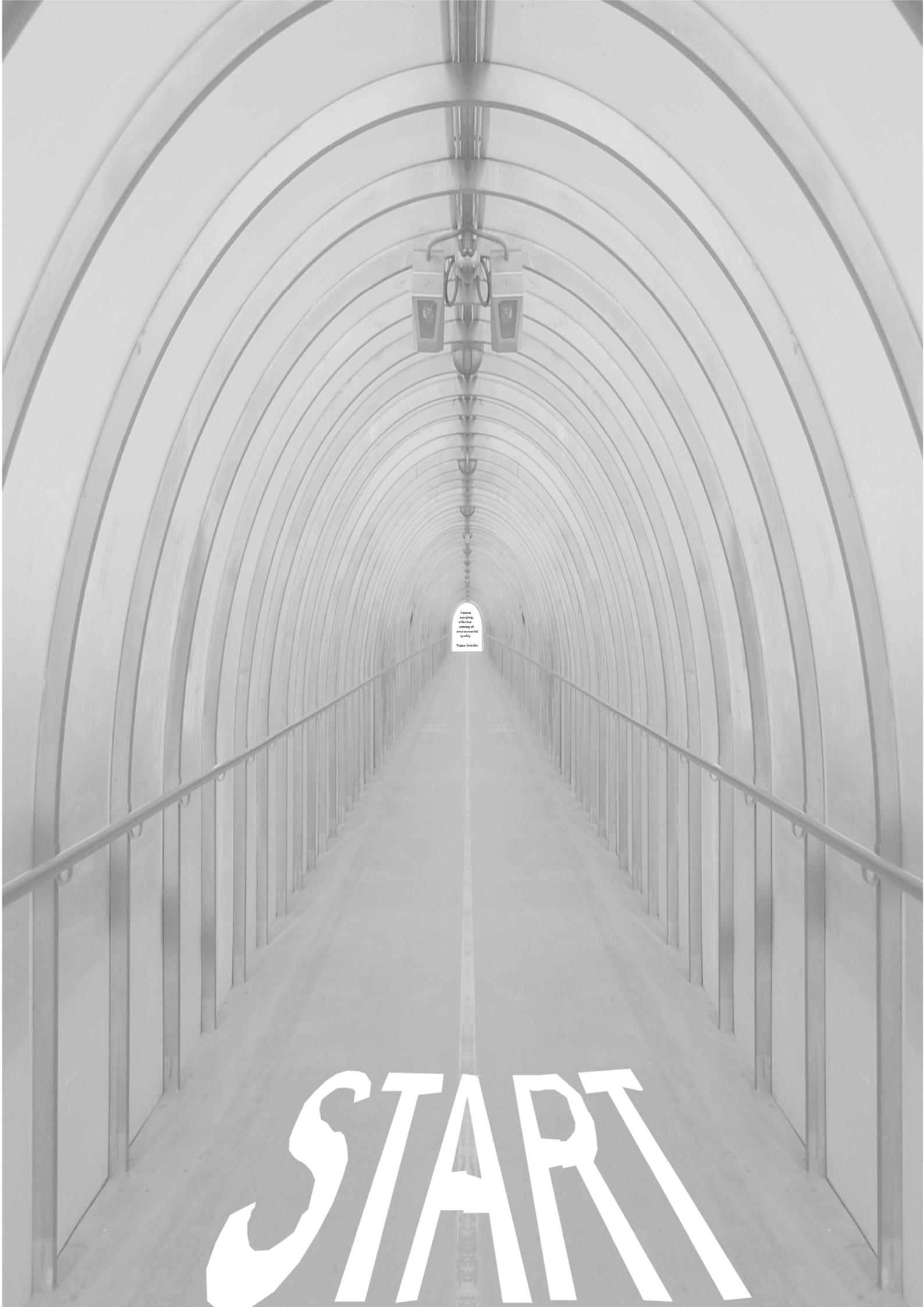
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Chapter 1

Introduction

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1.1. CHEMICALS IN THE ENVIRONMENT

In the modern world, humanity uses a countless number of manufactured chemicals for various purposes, including household products e.g. surfactants, preservatives, ingredients in personal care products, e.g. parabens, material additives like phthalates and bisphenol A to improve the quality of plastics, or flame retardants used, for example, in clothes, furniture, and heat insulation materials. Many of these chemicals have improved the quality of life, safety (flame retardants), protection against the spread of diseases like malaria (pesticides), and health (numerous drugs are used to treat illnesses). Many chemicals were, or are, used even though the risk they present to the environment or human health is not fully understood.[1] Chemicals enter the environment through air, waste or wastewater, where they can adversely affect the ecosystem and living resources, including humans. During the second half of the last century, public awareness grew of the risks that using synthetic chemicals could pose to the environment, and to humans through various exposure routes including inhalation, food and drinking water. To protect their citizens, authorities attempt to identify hazardous chemicals and install systems to regulate discharges and concentrations in the environment and food. Since water is essential to nearly all living creatures and is at the same time used to wash away a large part of the used chemicals, it is important to regulate and reduce contamination of the aquatic environment. This was initially arranged at a national level but the understanding that the issues needed to be managed at an international scale led in 1974 to the establishment of the international Oslo and Paris Convention (OSPAR) for the Prevention of Marine Pollution from Land-Based Sources in the north-east Atlantic area. OSPAR strives for reduction of the concentrations of chemical contaminants in the marine environment to as low as background levels.

Since protection of the North Atlantic is directly connected to the protection of fish and other aquatic life, OSPAR cooperates with other international organizations, including the International Council for Exploration of the Sea (ICES). In acting as scientific adviser, ICES provides advice to OSPAR on the effects and monitoring of hazardous substances, through a range of Expert Groups.

At the turn of the century, a European-wide approach under the Water Framework Directive (WFD)[2] identified a group of priority chemicals[3] that are harmful to the aquatic environment. EU Member States were required to take measures to achieve concentrations of the substances below agreed environmental quality standards (EQS). The EQS represent concentrations that are considered safe for the environment and human life.

Both OSPAR and WFD require national authorities to undertake monitoring of the quality of the aquatic environment under their management to confirm that environmental quality criteria are met and/or that the measures taken have the required impact and that levels of chemicals contaminating the environment exhibit downward trends. Although monitoring environmental quality may appear straightforward, measuring the concentration of a contaminant in an environmental sample can entail great difficulties, depending on the chemical as well as the matrix that needs to be monitored. For example, some environmental matrices have a variable bulk composition. In such cases, the apparent differences in contaminant concentration may not reflect a true difference in environmental quality. For a proper comparison of concentrations in space or time, it is important that they are measured in samples obtained from different stations that have the same composition, preferably consisting of one single phase. Guidelines on how to carry out monitoring have been developed.[4] They include sampling and sample pre-treatment procedures, analytical requirements and recommended analytical methods, quality

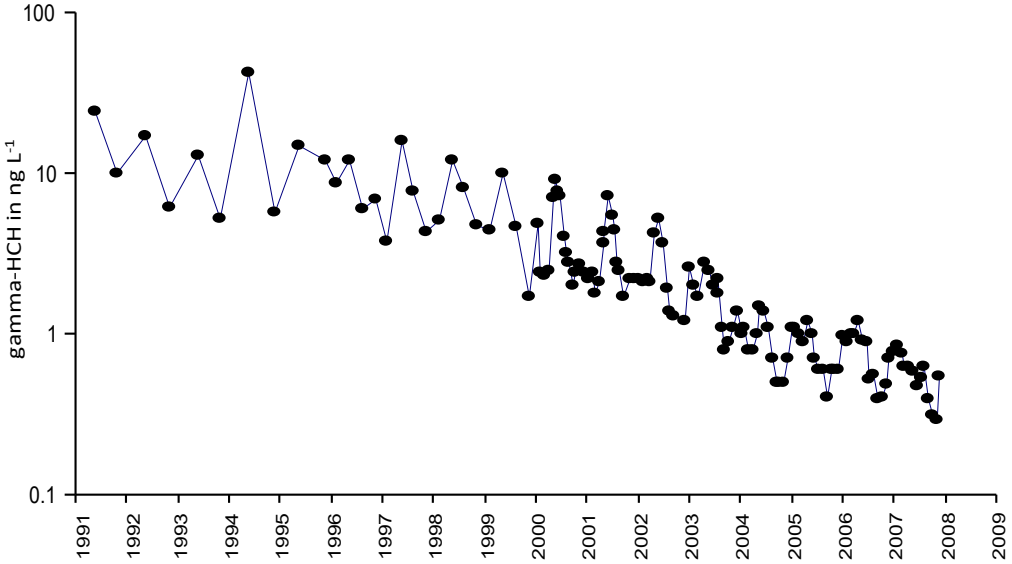

Figure 1 Seawater monitoring results of gamma-HCH (lindane, ng L^{-1}) in the Western Scheldt, near Hansweert.

assurance measures and directions for data interpretation and environmental quality assessment. In the following sections, monitoring of contaminants in various components the aquatic environment is discussed, with a focus on hydrophobic organic contaminants (HOC). Other types of contaminants are only briefly included when a further clarification of the subject under discussion is needed.

1.2. MONITORING THE AQUEOUS PHASE

Surface water is normally the transport medium from sources of contamination to receptors in the environment. Therefore, surface water is often considered as the most appropriate compartment in which to monitor contaminants in order to assess variations in environmental quality in time and space. This is essentially only the case for contaminants that are mainly present in the dissolved phase, i.e. substances that do not form complexes with other molecules or bind to particulate and/or dissolved organic matter. Particulate and/or dissolved organic matter content is generally expressed by summary parameters POC and DOC (the organic particulate and dissolved carbon, respectively) or as their sum, the total organic carbon (TOC). Substances dominantly present in the dissolved phase are inorganic ions (e.g. Na^+, K^+, Cl^-, NH_4^+, NO_3^- etc.). Organic molecules with a relatively large water solubility and low binding to TOC are also mainly present in the dissolved form. Gamma-HCH is a typical example of such a compound and its dominantly dissolved concentration can therefore be monitored in unfiltered water. Data from the Western Scheldt over two decades showed a 50-fold downward trend (Figure 1) as a result of prohibition of its use. This example confirms that for environmental monitoring a sample matrix where a compound is dominantly present in one definable phase (water in this case) can provide consistent results, allowing temporal (and special) trends to be detected. Such data were produced by in sample bottle extraction of 10 L water with pentane using the Continuous Batch Extractor developed at the National Institute of Coastal and Marine management/RIKZ.[5]

Using the Continuous Batch Extractor, it was also possible to determine PCB and PAH concentrations in water samples in the 10 pg L^{-1} range,[5] but the result was the sum of freely dissolved and adsorbed concentrations as no distinction could be made between freely dissolved and fractions bound to particulate matter. When the compound is mainly bound to TOC, water samples from the same water body containing different amounts of suspended matter will provide variable concentrations which are not likely associated with a different environmental quality.[6] The higher the contaminant's hydrophobicity (expressed as its octanol–water partition coefficient, K_{ow}), the larger fraction is bound to TOC. Contaminants with logK_{ow} >6 in whole water will be nearly completely bound to TOC. The distribution of a substance between dissolved and bound form depends on the hydrophobicity and the TOC content in the water column[6] (Figure 2). On the left side of the figure, contaminants with low K_{ow} are fully dissolved, where on the right contaminants are mainly DOC+POC bound. Depending on the TOC (DOC+POC) content, the transition range shifts to the left or right, at high or low TOC, respectively.

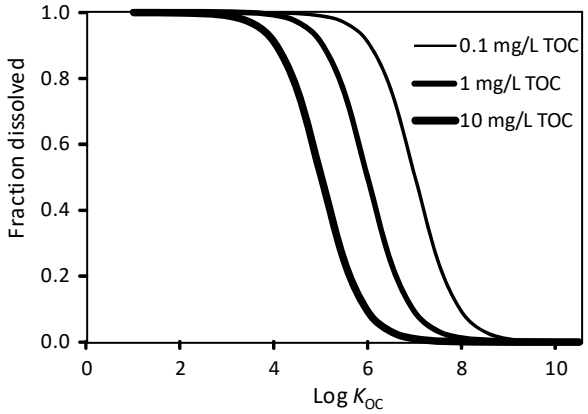

Figure 2 Fraction dissolved of a HOC in the water column in relation to its organic carbon–water partition coefficient (K_{OC}) for low, medium and high total organic carbon (TOC) content present in the water column. TOC is the sum of dissolved (DOC) and particulate (POC) organic carbon.

This is relevant for environmental quality assessment as the primary risk is reflected by the contaminant concentrations in the freely dissolved phase (C_w). Dissolved concentration in pore water better explained toxicity than whole sediment concentrations,[7] and were a good predictor of partitioning uptake by organisms.[8] This is because C_w has a defined basis, namely pure water and is therefore proportional to chemical activity, the driving force for partitioning processes (see 1.5.1). In other words, whole water is a variable and actually not a suitable matrix for monitoring chemicals with logK_{ow} >5, because the risk expressed in C_w, will remain largely constant if higher or lower amounts of TOC are suspended in water. Removal of SPM by filtration or centrifugation is not a viable option as it yields a water sample that still contains DOC, while with filtration (a portion of) the dissolved contaminants has been adsorbed by the filter.[5]

Despite the above, whole water concentrations of hydrophobic organic contaminants (HOC) are used for testing compliance with Environmental Quality Standards (EQS) within the WFD,[2] except for hexachlorobenzene and hexachlorobutadiene.[3] However, because analytical methods were often not capable of measuring concentrations in water as low as the EQS,[9] from 2013 the WFD made a switch to monitoring HOC in biota[10] and guidelines were developed.[11,12] OSPAR never considered water as a matrix for monitoring hydrophobic contaminants and has always focused on monitoring in biota and sediment. Both compartments strongly accumulate HOCs and resulting concentrations can generally be

more easily be quantified. However, these matrices are even more complex and heterogeneous than whole water and concentrations depend on many confounding factors.

1.3. SEDIMENT MONITORING

Sediment is one of the most variable matrices, showing large compositional differences in space as well as time. Fine grained sediment deposits in low-energy areas, whereas the bottom sediment is commonly coarse sand or gravel in areas with strong currents. Due to these dynamics, it is unlikely that the sampled sediment matrix has a stable composition in time and space. For adequate monitoring, variations in factors like bulk sample composition or seasonal effects should be avoided or corrected for by normalization to a standard composition.[13] For many years, there has been a considerable debate within OSPAR/ICES concerning methods and procedures to convert measured contaminant concentrations to a "standard sediment composition". Such correction would improve the data comparability and, therefore, the probability of detection of temporal as well as spatial trends.

Although results without normalization retain their analytical precision, this is "pseudo-precision" and has little meaning in an assessment or comparison to data from sediment samples having other compositions. Correction of the contaminant content for sediment composition always requires additional measured parameters to act as cofactor(s). Cofactors are parameter(s) that represent the bulk properties of the sediment in terms of composition and/or uptake capacity and are necessary to normalize concentrations to a fixed composition. Cofactors include particle size distribution, i.e. the fraction of fines or the Al and Li content representing the fine fraction, and the organic carbon (OC) content.[13-15] The normalization is done by inter- or extrapolation to a set cofactor concentration of a "standardized sediment" as described in Technical Annex 5 of the CEMP (Coordinated Environmental Monitoring Programme) Guidelines for Monitoring Contaminants in Sediments.[16] Within OSPAR, cofactors for the "standardized sediment" were set at 5% Al for metals and 2.5% OC for organic contaminants. These cofactors, for heavy metals as well as organic contaminants, are dominantly present in the fine fraction and therefore, the fractions <63 or <20 µm can be isolated from the bulk sediment by sieving before measurement of contaminants and cofactors. Sieving is frequently used as a first tier normalization to reduce the influence of compositional differences.[15,17] The second tier is then a further correction to the "standardized sediment" composition requiring only relatively minor inter- or extrapolation, compared to what would be needed for the original sediment. This approach was validated by demonstrating significant correlation between cofactors and contaminants in largely compositional different fractions of a single sediment artificially created by sieving and sedimentation. Concentrations of heavy metals demonstrated good correlations with clay, Al, Li and OC contents[13,14,16,18] and that of organotins and PCB were strongly related to the OC content.[14,18,19] Moreover, after normalizing the concentrations of individual fractions using OC content, no significant differences were observed.

This was not always the case for polycyclic aromatic hydrocarbons (PAH). Often the sieved particle fraction between 20 and 63 µm exhibited higher OC normalized concentrations than e.g. the fraction <20 µm or total sediment.[18] PAH are often associated to black carbon particulates originating form combustion, e.g. soot, or coal mining dust or waste, in addition to entering the aquatic environment in dissolved form. The native PAH in black carbon are strongly bound showing a limited release as confirmed by a two to three orders of magnitude higher K_{OC} compared to natural sediment organic matter.[20] Black carbon can be present in virtually all particle size fractions entering the aquatic environment through storm water runoff, depending on whether it originates from coke[21] or from imperfect combustion.[22] When applying a bioslurry treatment to degrade PAH to different size fractions of black carbon containing sediment from Milwaukee Harbor, PAH levels strongly reduced in the fine grained clay/silt fraction while PAH concentrations in the coal–derived material of larger particle size fraction were not affected.[23] Authors found that this observation was consistent with lower bioaccumulation in earthworms exposed to the fine grained clay/silt fraction before and after treatment. The decrease of concentrations by means of the bioslurry treatment indicates that concentrations in the fine material more closely reflect the bioavailable PAH than those in whole sediment or large size particle fractions. This is not always the case as fine grained sediment can also contain strongly bound fractions.[24] Consequently, normalizing PAH concentrations using OC may often provide an overestimation of the risk, but may not be cost–efficient because quality criteria may erroneously be exceeded. Organotin compounds[19] added to whole sediment were mostly sorbed by the fine-grained material and concentrations in fractions of larger size showed much less increase. Coarser fractions have a more variable composition and its cofactor contents are low. Consequently, removing this fraction by sieving leaves a more stable composition, better for <20 than <63 µm, which at the same time contain higher concentrations that present less of an analytical challenge and which better reflect sediment quality.

For HOC dominantly particulate bound, collection of suspended particulate matter (SPM) using sediment traps, continuous flow-through centrifuge or filtration has been suggested as an alternative to sediment monitoring.[25] SPM has been, or will become sediment, and is in a close contact with the water phase, likely reflecting water quality. At the same

time SPM has high clay and OC content suitable for applying similar normalization as for sediment. Consequently, it is rational to assess HOC concentrations in SPM in the same way as sediment. Obviously, application of SPM as a sample matrix for monitoring requires special facilities, i.e. sediment traps or continuous flow-through centrifuge, as well as sufficient SPM quantities to be present in the water column which is often not the case and season dependent.

1.4. BIOTA MONITORING

As for water and sediment, the ideal matrix for monitoring HOC in biota would have a constant composition over time and space. This is largely the case for Active Biota Monitoring (ABM) using blue mussels (*Mytilus edulis*); a method that allows evaluation of spatial as well as temporal trends, when taking seasonal variations into account.[26] Co-genetic mussels grown at a single location of low contamination were exposed in coastal waters at various locations. The concentrations of HOC in the mussels could mostly be measured and exhibited a spatial distribution in the Dutch marine environment that was consistent with expectations,[27] even with the local differences in environmental variables. Despite the starting mussels being different every year, temporal trend detection is applicable if exposed in the same season. However, ABM is limited to areas where mussels can be exposed.

Within OSPAR, monitoring of HOC in biota is usually applied using fish livers or bivalves (mussels) tissue.[28] Fish sampling can be linked with fish disease monitoring. Monitoring a single fish species over the whole convention area is not possible and guidelines[29] list a number of suitable species, as well as required numbers and sex, i.e. female. The size range should be constant from year to year and spawning periods should be avoided with sampling preferably taking place in autumn. The monitoring guidelines also include analytical procedures and QA procedures.[29] Member states report all data to the ICES database (http://www.ices.dk/marine-data/data-portals/Pages/DOME.aspx) where data are also accessible. Following an assessment manual,[4] data are assessed by OSPAR working groups through trend analysis and checking if the upper 90% confidence limit of the last year's trend result complies with set environmental assessment criteria (EAC). For HOC in fish, this assessment is generally done after applying lipid normalization.

Within the WFD, EQS were set for biota, for PAH in crustaceans and mollusks, for dioxin(-like) substances in fish, crustaceans and mollusks, and for all other priority HOC the EQS are set in fish.[10] All EQS were set on a wet weight basis. A guideline is provided for implementation which includes a form of normalization to a "standardized fish"[11]. In this normalization, corrections for lipid content and/or wet weight were made, as well as conversion to trophic level 4 in order to normalize HOC's biomagnification. The approach allows a more balanced assessment against the EQS and different fish species used in the monitoring should exhibit limited differences. However, in addition to the actual measurement of the concentrations in fish, the procedure requires additional measurement of lipid content, dry weight, $\delta^{15}N$ in the sample and the food source, and knowledge of the trophic magnification factor, which may vary between different ecosystems.

In addition to the above issues, the guidelines[11] suggest that to perform biota monitoring with the best possible species and approaches, a substantial number of criteria need to be considered. Selected species should be abundantly present; widespread over the catchment requiring them to be adaptable to a wide range of environments, in order to avoid the need to use multiple species. Although such ideal species for monitoring can thrive in all conditions, it should be sedentary to reflect the local concentrations of contaminants. Further, the species must live long enough to accumulate contaminants, have sufficient tissue mass for analysis and be of no socio-economic interest or have a protected status. And last, but not least, they should be of a size and trophic level to be relevant to the protection goal. It has proved to be difficult to find species that meet all those criteria and likely even more difficult to catch that ideal species in the same size range for consecutive monitoring years, a requirement for adequate biota monitoring.

Other approaches are, however, allowed. Paragraph (17) in Directive 2013/39/EU[10] establishing the EQS for biota gives flexibility to member states to apply an EQS for an alternative matrix to adapt to what is possible or to connect to preexisting monitoring programs "*provided that the level of protection afforded by the EQS and the monitoring system applied by the Member States is as good as that provided by the EQS and matrix laid down in this Directive"*.

Interestingly, the following paragraph (18) in this Directive reads, "Novel monitoring methods such as passive sampling and other tools show promise for future application, and their development should therefore be pursued", which is precisely the subject of this thesis. When evaluating passive samplers, e.g. sheets of soft polymer, as an alternative for biota monitoring, it seems they meet many of the above criteria for monitoring species. An abundant presence of passive samplers can be regulated with application everywhere in all catchments, even where biota cannot live, while further passive samplers do not migrate. The mass/uptake surface and exposure time is adjustable to assure sufficient accumulation for adequate analysis for which the results only need a conversion method to a required trophic level or another way to be relevant for the protection goal, e.g. conversion of the EQS into units provided by passive sampling.

1.5. PASSIVE SAMPLING

At the end of the last century, passive samplers emerged in the toolbox available for environmental monitoring of HOC in water. The most widely known passive sampler is the semi–permeable membrane device (SPMD)[30] which is constructed of a layflat low density polyethylene (LDPE) tube filled with triolein, the main (65%) lipid in olive oil but also present in the lipid of living organisms. When initially applying SPMDs it was not clear that, not only the lipid, but also the LDPE was largely contributing to the uptake capacity of the sampler. Although SPMD are at present still widely used because of their commercial availability, they are gradually being replaced by single phase polymeric samplers constructed from LDPE or silicone. Single phase samplers work according to the same principle but are less fragile (lipid cannot leak during exposure and/or extraction) and the sampler-water exchange of a single sampler can be described by simpler modeling.

When exposed in the aquatic environment, samplers can be regarded as a kind of "artificial organism", absorbing HOC at a rate proportional to their aqueous free dissolved concentration. Uptake is driven by the higher solubility of HOC in the sampler compared to water, which is expressed in the sampler–water partition coefficient (K_{PW}). The advantages of passive samplers versus organisms are their constant properties, while for organisms, local conditions, differences in season with associated biological activity, will always influence their uptake and final internal concentrations. During the aqueous exposure, the uptake rate of passive samplers mainly depends on the physical circumstances, like hydrodynamics and temperature. Uptake of HOCs by passive samplers is mostly controlled by diffusion through the water boundary layer (WBL), a layer on the surface of the sampler where diffusion dominates over advection, the thickness of which depends on the local hydro dynamical conditions. Uptake slows down towards equilibrium, which takes longer for HOC with greater K_{PW} . In the following section first the principles of equilibrium passive sampling are discussed, later followed by non–equilibrium sampling.

1.5.1 Chemical activity

For monitoring of environmental quality actually all kinds of concentrations are measured in various matrices. But an environmental concentration is not a substitute for environmental quality. When comparing with measurement of heat, in many situations the contaminant's concentration is more like the number of calories in a sample, while only the ratio of the number of calories in the sample and its heat capacity makes the temperature, representing the actual risk of burning your fingers. Consequently, the same number of calories in objects of different heat capacity does not mean an equal risk of burning. That is what makes a thermometer so useful. The calorie content – heat capacity ratio is closely comparable with chemical activity.[31]

Chemical activity (CA), in a simple but useful form, equals the ratio between matrix's HOC concentration and its HOC uptake capacity.[32] If the various matrices in an ecosystem are all at equilibrium, the HOC's CA would be equal in all matrices but HOC's concentrations would be very different in e.g. water, air fish and sediment, corresponding to the matrices' uptake capacities.

The role of uptake capacity can be understood via partition coefficients, e.g. for sediment:

$$K_{\mathrm{SED}} = \frac{C_{SED}}{C_{\mathrm{W}}} \qquad 1$$

where K_{SED} is the HOC's sediment–water partition coefficient,

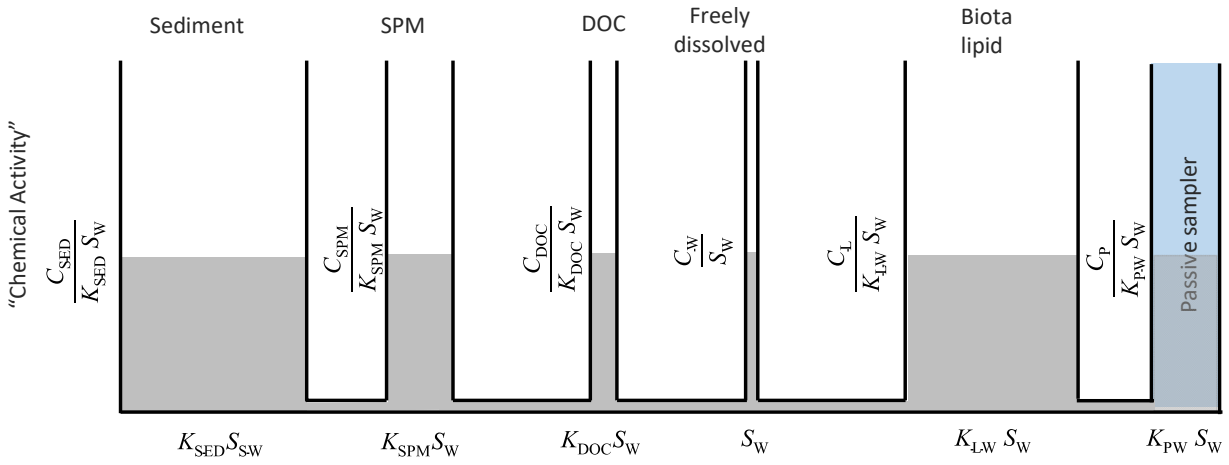

Figure 3 How HOC concentrations in various environmental matrices compare when in equilibrium with each other. For each matrix the x–direction represents it's capacity, expressed as the product of matrix–water partition coefficient (L kg^{-1}) and solubility (kg L^{-1}). The y–direction, "filling height", reflects CA on a 0–1 scale, indicating chemical activity (CA) as the ratio of HOC's concentration in the matrix and matrix's uptake capacity for the HOC. i.e. aqueous solubility (kg L^{-1}) and is maximum capacity. Consequently, with CA being equal for all matrices the concentrations (gray surface area x×y) are highest for biota and sediment, and lowest as freely dissolved.

and C_{SED} and C_W the equilibrium concentrations in sediment and pure water, respectively. A known K_{SED} can be used to estimate C_W from C_{SED}. However, with K_{SED}'s units being L kg^{-1}, K_{SED} is also the volume of water (L) containing a HOC mass equivalent to one kg of sediment. The uptake capacity of a HOC in water equals its solubility (S_W) and consequently sediment's uptake capacity (U_{SED}) equals:

$$U_{SED} = K_{SED}\, S_W \qquad 2$$

Except for the freely dissolved phase, eq 2 applies to all other matrices. Consequently, for all matrices *CA* can be expressed as the ratio of the HOC concentration in the matrix to the HOC uptake capacity of the matrix. When equilibrium exists between the matrices in an ecosystem, *CA* is equal in all matrices, including in passive samplers that have been exposed until equilibrium has been reached:

$$CA = \frac{C_{SED}}{K_{SED}S_W} = \frac{C_{SPM}}{K_{SPM}S_W} = \frac{C_{DOC}}{K_{DOC}S_W} = \frac{C_W}{S_W} = \frac{C_L}{K_{LW}S_W} = \frac{C_P}{K_{PW}S_W} \qquad 3$$

where the subscripts L and P, indicate biota lipid and passive sampler polymer, respectively. In Figure 3 the implication of eq 3 is presented in a more perceptive way. In real ecosystems, without strict phase boundaries, there is often no equilibrium and *CA* will not be equal in all matrices, e.g. for biota biomagnification or metabolism of HOC may influence *CA* if faster than the exchange between matrices.

It is nevertheless illustrative to evaluate what eq 3 means when monitoring *CA* as a reflection of environmental quality. Clearly the ideal matrix to monitor *CA* would have the highest concentration and a defined or fixed uptake capacity that is not subjected to natural variability. Overall *CA* precision is assured if both numerator and denominator in eq 3 have adequate precision. Properties of sediment, SPM, DOC, and also biota, have a natural variability, and only pure water and the polymer of the passive sampler are adequately defined and/or constant. Isolation of the pure water phase is not feasible for HOC,[5] and if that would be possible, the concentrations and/or the isolated volume would be too low to measure the concentrations of HOC. Because of the high accumulation of HOC in a sampler's polymer matrix, only passive sampling combines sufficient sensitivity with a fixed uptake capacity. Although a passive sampler can function as a kind of thermometer for environmental quality,[33] it is not yet an accepted approach and concentration conversion to another matrix is required. Passive sampling uptake is typically converted to C_W, which has shown good relations with concentrations in mussel,[27,34] but the obtained C_W was also further converted to lipid.[8] Principally, equilibrium concentrations of HOC in passive samplers can actually be converted to any matrix provided that adequate partition coefficients are known and linear sorption isotherms apply for that matrix.

1.5.2 Passive sampling of multiple media

In the previous section the distribution of HOC among various matrices was considered for an ecosystem at equilibrium, but passive sampling can also be used to investigate disequilibrium. Note that when multiplying eq 3 by S_W, all terms will represent C_W:

$$C_W = \frac{C_P}{K_{PW}} = \frac{C_{SED}}{K_{SED}} = \frac{C_{SPM}}{K_{SPM}} = \frac{C_{DOC}}{K_{DOC}} = \frac{C_L}{K_{LW}} \qquad 4$$

and equilibrating passive samplers with the matrices independently will reveal the directions of spontaneous diffusive HOC exchange between the matrices, e.g. indicating if the sediment is a source or sink for HOC in the water phase. Such conclusion can also be drawn from C_P only, but conversion to knowing C_W, but will also assist modelers in flux estimation.

Another interesting option is multiplying the terms in eq 3 by both S_W and K_{LW}, giving:

$$C_L = C_P \frac{K_{LW}}{K_{PW}} = C_W K_{LW} = C_{SED} \frac{K_{LW}}{K_{SED}} = C_{SPM} \frac{K_{LW}}{K_{SPM}} = C_{DOC} \frac{K_{LW}}{K_{DOC}} \qquad 5$$

where the ratio K_{LW}/K_{PW} is actually the lipid–polymer partition coefficient K_{LP}, which can also accurately be determined directly.[35] Comparing lipid converted concentrations in water or sediment equilibrated samplers with lipid-based biota concentrations allows assessment of bioaccumulation and biomagnification.

Principally, it is also possible to express HOC concentrations in equilibrated samplers as concentration in sediment[36], SPM or DOC, but the properties of these materials are very variable, even if expressed on only their OC content. For lipids, on the other hand, it was shown that K_{LP} did not significantly differ for various lipid types.[35] Expressing the HOC concentration in various environmental media on a lipid basis to compare levels is an approach transparent for scientist, regulators and the public.[37]

1.5.3 Uptake and equilibrium

The above applications all use equilibrated passive sampler concentrations, but attaining equilibrium with the sampled medium requires time. In laboratory trials, agitated sampler–sediment, or sampler–SPM (if collected in sufficient amounts) exposures, equilibrium can be attained in a six-week exposure period due to the intensive contact. However, for field-exposed passive samplers in surface waters, equilibrium times are much longer and for HOC with $\log K_{OW} > 6$ it is practically not possible to achieve equilibrium and quantification of uptake kinetics is required. Sampler uptake, as well as release can be described by a first-order uptake kinetics model:[38]

$$C_P^t = C_P^0 + (C_P^\infty - C_P^0)\{1 - \exp(-k_e t)\} \quad 6$$

where C_P^0, C_P^t and C_P^∞ are the concentrations in the sampler at the start of the exposure, at time t and after infinite time, respectively, and k_e is the exchange rate constant (Note that C_P^∞ equals C_P used in previous equations). For measuring uptake, C_P^0 in samplers is zero and C_P^∞ is obtained by:

$$C_P^\infty = \frac{C_P^t}{1 - \exp(-k_e t)} \quad 7$$

Clearly, if no equilibrium is attained, it is a prerequisite to determine k_e. To do this, it was first proven that the permeability of polymers such as silicone and LDPE is high and that uptake is dominantly controlled by the mass transfer across the water boundary layer,[39] quantified as the diffusion distance per unit of time (k_W). The product of k_W and samplers surface area (A) gives an imaginary water volume that is extracted by the sampler per unit of time: the sampling rate R_S. The volume units of R_S relate to the sampler's water volume capacity, i.e. K_{PW} and mass of the sampler (m_P). Consequently, the exchange rate constant k_e equals the ratios:

$$k_e = \frac{k_W A}{K_{PW}\, m_P} = \frac{R_S}{K_{PW}\, m_P} \quad 8$$

Because, in given hydrodynamic conditions, R_S is only moderately affected by slower diffusion for compounds of increasing molecular size, k_e is largely determined by the sampler's water volume capacity (denominator). A relation of R_S with HOC's properties was found in the molecular mass (M), i.e. $R_S = B\, M^{-0.47}$, with B as proportionality factor containing the local hydrodynamic conditions and unit conversions. Combining this relation with eq 7 and 8 gives:

$$C_P^\infty = \frac{C_P^t}{1 - \exp\left(\frac{-Bt}{M^{0.47} m_P K_{PW}}\right)} \quad 9$$

The influence of hydrodynamic conditions on the water–sampler exchange collected in B, is equal for uptake and release. The determination of B is accomplished by recording the release of compounds dosed to the sampler prior to exposure. These compounds, performance reference compounds (PRC), do not occur in the environment and consequently C_P^∞ will be known, i.e. equal zero, and eq 6 transforms to:

$$C_P^t = C_P^0 \exp(-k_e t) \quad 10$$

Replacing k_e as for eq 9, after rearrangement the retained fraction PRC (f_m) can be modeled by:

$$f_m = \exp\left(\frac{-Bt}{M^{0.47} m_P K_{PW}}\right) \quad 11$$

while the retained fraction from measured data (f_{exp}) after field exposure is given by:

$$f_{exp} = \frac{C_P^t}{C_P^0} \quad 12$$

The f_m are fitted to f_{exp} for all PRC by non-linear least squares regression (NLS) with B as adjustable variable. To obtain an accurate estimate of B, the PRC should be selected such that they cover a wide logK_{PW} range. These should include low logK_{PW} PRC that fully dissipate during deployment ($f_{exp} \rightarrow 0$), as well as PRC with higher logK_{PW} showing different degrees of dissipation, and further very hydrophobic PRC that only negligibly dissipate ($f_{exp} \approx 1$) under the given field conditions. With this range of f_{exp} and using K_{PW},[40,41] B can be estimated fitting with the modeled values.[42]

Subsequently HOC's C_P^∞ for the aqueous phase can be calculated for situations where equilibrium was not attained (eq 9). This C_P^∞ or that from equilibrations with sediment, SPM, or even fish tissue, can then be used to calculate the C_W for the aqueous or aqueous equivalent C_W for other matrices (eq 4). Furthermore, for matrices the sampler was exposed to, C_P^∞ can be converted to lipid basis by means of K_{LP}, providing C_L equivalent concentrations for those matrices, (eq 5). Of course, such matrix–equivalent HOC concentrations only apply when measured and predicted matrices are in equilibrium. For example, C_L converted from aqueous sampling indicates the lipid based HOC concentration in biota for the case that biota would be in equilibrium with the sampled water. Differences with observed concentrations may be attributed to organisms' internal processes like biomagnification or metabolism. The aqueous equivalent lipid-based HOC concentration may be an excellent representative of environmental quality, where measured concentrations in the biota on a wet-weight basis are more related to the risk for predators and food safety.

1.6. SCOPE OF THIS THESIS

This thesis investigates the passive sampling technology and, together with a number of parallel papers, provides a complete methodology for passive sampling of HOCs in different compartments of the aquatic environment: water, sediment and biota, with required sampler–water and sampler–lipid partition coefficients. Throughout this work, samplers constructed of silicone were normally used, but most of the methodology also applies to other polymers with sufficiently high permeability like polyethylene, for which also K_{PW} values are provided. Passive sampling was introduced because its partition-based uptake was mimicking partition-driven uptake by organisms, which is considered to be a good measure for HOC exposure and reflecting environmental quality.

The activities on passive sampling started after discovering

the limitations of the measurement of HOC in total water as discussed in Chapter 2. Due to the strong sorption of HOC to all organic carbon-containing dissolved and non-dissolved material, HOC's concentration in water strongly reflects the presence of such material rather than the water quality.

Passive sampling turned the strong affinity of HOC to all non–dissolved material into an advantage by large HOC accumulation. With the state of published and non-published knowledge at that time, a monitoring program using passive sampling was started in the year 2001. The program was coupled to the routine Active Biological monitoring (ABM) or *Mussel-watch* program, sampling at eight stations in Dutch coastal waters. The result of the first five years are reported and discussed in relation to ABM in Chapter 3.[27]

Like in surface water, the presence of non–dissolved material may also hinder the determination of HOC's freely dissolve concentrations when determining their sampler–water partition coefficients. Chapter 4 reports on the use of the co-solvent method, which was applied earlier for sediment–water partition coefficients.[43] Sampler–water partition coefficients (K_{PW}) were determined in pure water and in a range of methanol fractions in water. Via a log-linear regression of sampler–water, and sampler–methanol/water partition coefficients versus the molar fraction methanol, K_{PW} is determined. Validation is achieved by agreement of this K_{PW} with that measured for water only.[40]

In Chapter 5 the isotropic behavior of the sampler–water exchange is confirmed and a relation derived between sampling rate and molecular mass.[44] Both make it possible to apply compound-specific sampling rates from measured release of compounds dosed to the sampler prior to exposure.

With passive sampling in sediments under agitation in the laboratory depletion may occur if the capacity in the contained amount of sediment is too small compared to that of the sampler. Chapter 6 describes a new approach where passive samplers are equilibrated with sediment in largely different sampler–sediment ratios, actually taking advantage of depletion to determine HOC's C_W through C_P^∞, as well as the fraction releasable from the sediment.[45]

Chapter 7 reports on the determination of polymer–lipid partition coefficients (K_{PL}) of about 80 HOC, as well as uptake and diffusion of lipid in polymers. It is further investigated whether lipid absorbed by the polymer affects the K_{PL}.[46]

Methods for passive sampling of HOC in fresh lean and lipid-rich fish tissue with a view of attaining equilibrium before the tissue is deteriorated is investigated and reported in Chapter 8, also introducing the application of PRC for quality control on equilibrium attainment.[47]

The work in previous chapters was combined in an investigation on how monitoring lipid-based HOC concentrations (C_L) in fish species relate to C_L derived from aqueous passive sampling. Hereto various fish species of different trophic level were sampled parallel to aqueous passive sampling at three locations in the Czech Republic and Slovakia: a closed fishpond and two contaminated river sites. The results are used to assess trophic magnification in terms of the C_L of the water phase as discussed in Chapter 9. Finally, the main results of this thesis are critically discussed as well as the perspective of passive sampling for its application as a method for monitoring HOC.

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